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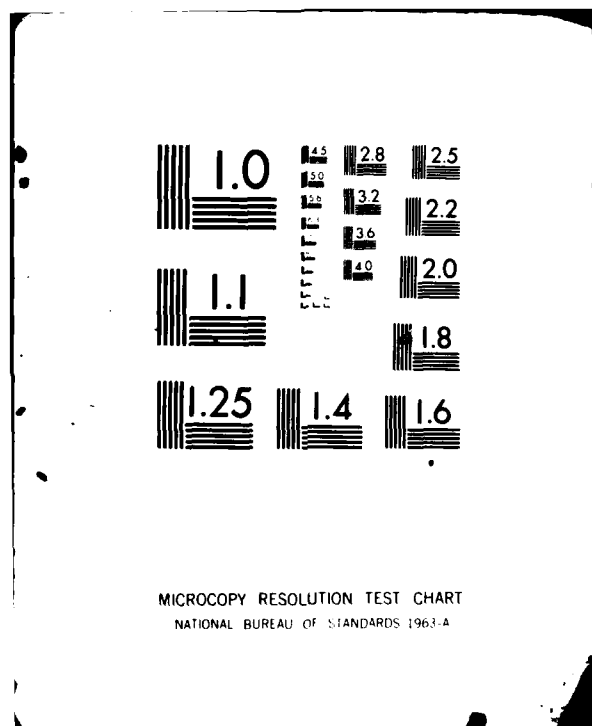
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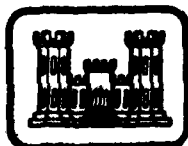
**IDENTIFYING AND DETERMINING
HALOCARBONS IN WATER
USING HEADSPACE GAS CHROMATOGRAPHY**

Daniel C. Leggett

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distribution ratios are determined experimentally. The method is absolute, unlike solvent extraction, resin sorption, purge and trap, and conventional headspace analysis, which require standard additions to correct for incomplete recovery.

The use of the technique to analyze chlorinated water samples for haloforms revealed a potential problem in their analysis. Haloforms continued to form for 24 hours, even after destruction of chlorine residuals with thiosulfate. Maximum haloform concentrations were observed in undechlorinated samples only after a 48-hour aging period.

PREFACE

This report was prepared by Daniel C. Leggett, Research Chemist, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by In-House Laboratory Independent Research Budget, Subactivity P611101, and Civil Works Research and Investigation Project, Work Unit CWIS 31281, Techniques for Land Treatment of Wastewater.

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IDENTIFYING AND DETERMINING HALOCARBONS IN WATER USING HEADSPACE GAS CHROMATOGRAPHY

Daniel C. Leggett

INTRODUCTION

Chlorination is a well-established method of disinfecting water for drinking and of disinfecting municipal wastewater prior to disposal. The recent discovery that persistent chloro-organic molecules are formed in this process¹⁻⁵ has brought it under scrutiny. While the health effects of chlorination are still being evaluated and alternative disinfection methods are being sought,^{6,7} attempts are being made to reduce the formation of chlorinated organics by making process modifications⁷⁻⁹ and to reduce their levels after formation by using advanced treatment processes.^{7,10-18}

An interim solution to the problem has been to continue chlorinating, with limits set on concentrations of certain products. The U.S. Environmental Protection Agency has set an arbitrary limit of 100 ppb of trihalomethanes in finished drinking water.¹⁹

Methods are thus needed for routinely monitoring levels of trihalomethanes in water. A number of techniques have been used for their determination: purge and trap,^{17,20,21} resin sorption,^{4,22,23} solvent extraction,²⁴⁻²⁶ direct injection,²⁷⁻²⁹ and headspace analysis.³⁰⁻³³

Multiple equilibration headspace analysis,³⁴ in conjunction with electron capture gas chromatography, is a sensitive method requiring little auxiliary equipment. In this report I describe the use of this method, some of its advantages, and some of its applications for determining volatile halogen compounds associated with water and wastewater treatment.

METHOD

Multiple equilibration headspace analysis was conducted as described by McAuliffe,³⁴ using hydrocarbon-free nitrogen as the equilibrant. The water samples to be analyzed were equilibrated with gas in a 50-ml gas-tight syringe (Hamilton) with a standard luer hub and removable stainless steel needle. The syringe, with its plunger removed, was completely

filled with the water sample. The plunger was inserted and the syringe turned over, expelling any remaining gas bubbles through the needle. Water was expelled until only the desired volume remained, usually 25 ml. An equal volume of gas was added through the needle by puncturing the septum on a gas chromatograph. The water and gas were shaken vigorously by hand for three minutes, during which time water sealed the needle, preventing entry of outside air. After the water in the needle was expelled, at least 20 ml of gas was forced through a gas sampling loop and injected into the gas chromatograph. The sample was re-equilibrated repeatedly (three to seven times) with fresh nitrogen.

The halocarbon concentrations in the sample were determined by measuring the areas under the chromatogram peaks by manual triangulation for all equilibrations and plotting them vs equilibration number on semi-log paper. In this mathematical treatment, derived by McAuliffe,³⁴ a straight line of best fit is drawn through the points. Any two successive points are used to determine the slope. The gas/water distribution coefficient equals the slope minus one, and the original water concentration equals the intercept divided by the distribution coefficient.

To test this method I collected tapwater and wastewater samples in 300-ml glass BOD bottles containing 0.5 g of sodium thiosulfate (to destroy chlorine residuals). The bottles were carefully filled, leaving no air space.

Gas chromatographic analyses were conducted on a Perkin-Elmer Model 900 GC with a titanium tritide source operated in the pulsed mode (50- s interval). The halogenated organics were separated on Carbowax 400/Porasil C Durapak (Water's Associates). The material obtained from the manufacturer was washed with acetone and oven-dried prior to packing into 1/8-in. stainless steel columns. The columns and detector were maintained at 105°C, and the carrier gas was oxygen-free (<0.5 ppm O₂) or ultrapure nitrogen (used without further purification) flowing at 15 ml/min. Headgas samples were injected with a 1.80-ml Teflon loop and Perkin-Elmer gas sampling valve.

Working standards for qualitative and semi-quantitative analyses were prepared in reagent grade methanol (10^{-4} to 10^{-5} v/v). A 10^{-1} aliquot

of working standard was diluted in 5 to 25 ml of halocarbon-free water in a 50-ml gas-tight syringe. (Halocarbons were removed from distilled water by bubbling hydrocarbon-free nitrogen through it.) For quantitative analysis, working standards were prepared by diluting EPA purgeable organics in halocarbon-free well water and were used immediately.

DISCUSSION

Figure 1 shows the characteristic depletion in successive equilibrations of several halocarbons added to distilled water. Note that some peaks disappear more rapidly than others. This is one advantage of this method, because the rate of disappearance of any compound is directly related to its distribution coefficient. Distribution coefficients can be used to establish or confirm the identity of compounds. The distribution coefficients obtained here are a function of the relative volumes of gas headspace and water during the analysis, but they can be converted to dimensionless, volume-based, Henry's Law constants by dividing the value by the ratio of gas/liquid volumes. For example, if we equilibrate 10 ml of water with 40 ml of nitrogen gas and obtain a distribution coefficient of 2.0, the Henry's Law constant is $2 \div 4$ or 0.5. Henry's Law constants for a number of compounds have been tabulated,^{15,35,36} and when they are not available, Dilling's procedure³⁵ can be used to estimate values. The combination of electron capture response, Henry's Law constant and gas chromatographic retention time probably provide sufficient evidence of compound identity without resorting to independent confirmatory methods, such as the use of multiple columns and detectors or mass spectrometry.

Another advantage of this method is that halocarbon concentrations above the linear range of the electron capture detector can be analyzed simply by performing additional equilibrations. As long as two are known to be in the linear range, the extrapolation procedure can be used to find the concentration.

Multiple equilibration also has the advantage that matrix effects are circumvented, since extraction efficiency does not affect calculation of the concentration. The only requirement is that the system be at equilibrium when the analysis is performed.

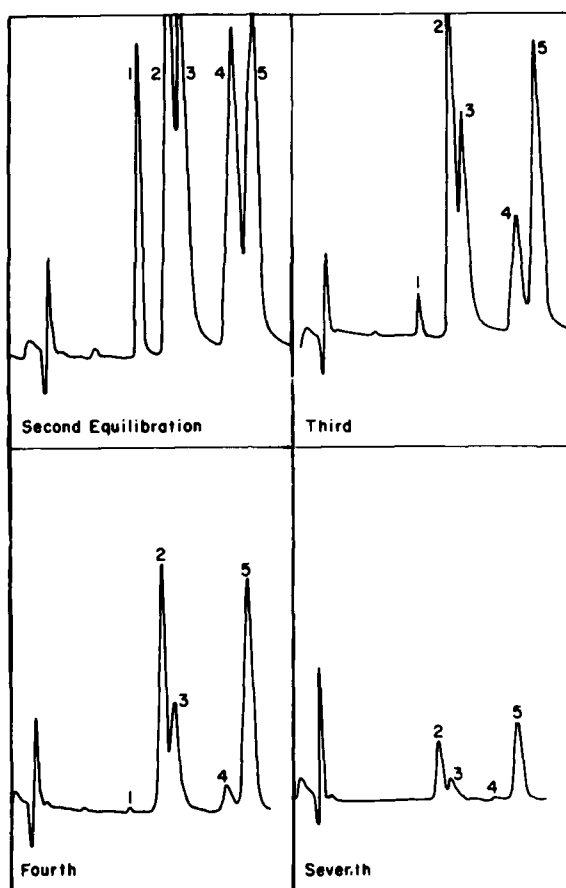


Figure 1. Behavior of some halocarbons in distilled water during multiple equilibration with nitrogen (volume of gas, 40 ml; volume of liquid, 10 ml). 1) CCl_4 , 2) CHCl_3 , 3) $\text{CHCl}=\text{Cl}_2$, 4) C_2Cl_4 , 5) 5 CHBrCl_2 .

An advantage of using electron capture detection is that coulometric responses may be obtained for some compounds; that is, complete ionization can occur in the detector, and the peak area response in coulombs (A·s) is then an absolute measure of the number of moles of substance present. The number of coulombs is directly related to the number of moles by Faraday's Law (96,500 coulombs = 1 mole). Lovelock³⁷ extended this concept by using two identical electron capture detectors in series. This enables one to determine the ionization efficiency, so that even for a compound displaying less than coulometric response, quantitative analysis can be

performed without reference to a calibration standard.^{37,38} The obvious advantage to this is that it obviates accurate preparation of low-level halocarbon standards in water, which is difficult at best. In preliminary work, carbon tetrachloride and methyl iodide were found to be perfect electron absorbers, matching the theoretical 96,500 coulombs per mole.

A typical multiple equilibration chromatogram of local tap water is shown in Figure 2. Chloroform (CHCl_3) and bromodichloromethane (CHBrCl_2) are likely attributable to chlorination of the town water supply, which comes from a surface impoundment. Trichloroethylene (C_2HCl_3) and trichloroethane ($\text{C}_2\text{H}_3\text{Cl}_3$) have not been associated with chlorination, but both are common industrial solvents. Trichloroethylene is not further reduced in the fourth equilibration, partly because of contamination by laboratory air during the analysis. Other contaminants in the laboratory air were not present in sufficient concentration to interfere with the analysis. It was not determined whether the traces of Freons 12 and 11 (Peaks 2 and 3) were due only to their natural abundance in the atmosphere³⁹ or were due to contamination from other sources as well.

Figure 3 shows the effect of adding 20 ppm bromide ion as sodium bromide to tap water. The water was not dechlorinated before the bromide was added. After the bromide was added, the mixture was allowed to sit for 25 minutes until the single equilibration analysis was begun. The before-and-after chromatograms show that although the chloroform concentration did not increase measurably in that time, the concentration of the three bromotrihalomethanes increased substantially. This may be due to the oxidation of part of the bromide to hypobromite, which is a more facile halogenating agent than hypochlorite.^{1,33,40}

When chlorine is added to natural waters, the relative amount of each of the possible haloforms is determined by the relative halogen concentration in the water.⁵ The mechanism of the reaction is discussed in organic chemistry textbooks and has been reviewed by Morris.⁴¹

Chromatograms of tap water headspace (Fig. 2 and 3) showed an unidentified peak eluting before carbon tetrachloride. I observed this peak in chromatograms of tap water and chlorinated sewage effluents and found it to be temperature-sensitive, decreasing in magnitude as the gas chromatograph injector temperature was increased. Its magnitude increased when the water

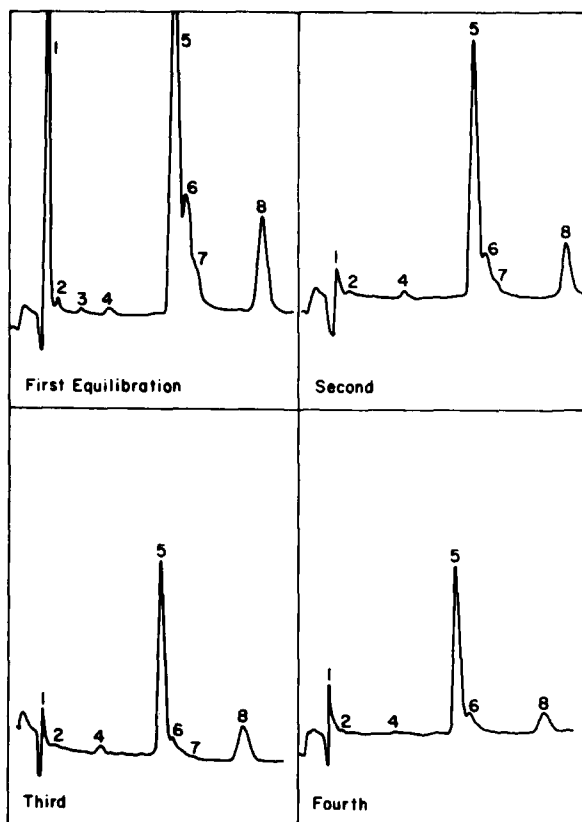
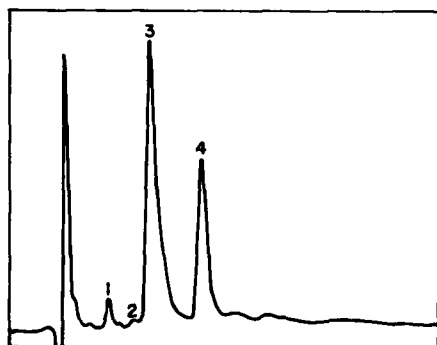
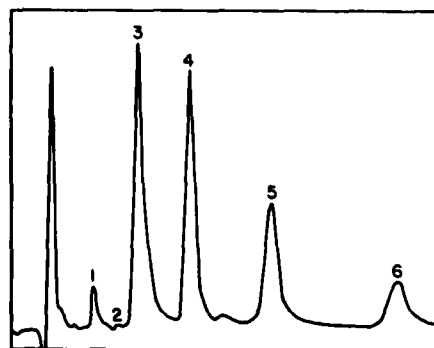


Figure 2. Multiple equilibration of tap water from Hanover, N.H. (volume of gas, 40 ml; volume of liquid, 10 ml). 1) O_2 , 2) CCl_2F_2 , 3) CCl_3F , 4) unknown, 5) $CHCl_3$, 6) $CHCl=CCl_2$, 7) CH_3-CCl_3 , 8) $CHBrCl_2$.



a. Hanover tap water, 4 November 1976.



b. Tap water 25 minutes after adding 20 ppm Br^- .

Figure 3. Effect of bromide ion in the presence of chlorine on formation of haloforms. 1) Unknown, 2) CCl_4 , 3) $CHCl_3$ and $CHCl=CCl_2$, 4) $CHBrCl_2$, 5) $CHBrCl$, 6) $CHBr_3$.

was spiked with ammonium and hypochlorite, but the peak was absent from chromatograms of solutions dechlorinated with thiosulfate. These results suggest that the peak was due to a chloramine (probably nitrogen trichloride), although authentic standards were not available for comparison.

Figure 4 reveals a potential problem in analyzing for haloforms in water. In this case the water was not dechlorinated prior to multiple equilibration analysis. The apparent Henry's Law constant for chloroform when fresh tap water was equilibrated was 0.054; in aged tap water it was 0.159, which is close to the expected constant.^{12,35} Evidently the chloroform concentration in solution increased during the analysis. This effect was also observed in analyses of samples aged for several hours after chlorine residuals had been destroyed. This may be due to the slow hydrolysis of trihalogenated chloroform precursors, such as tri-, tetra-, penta-, and hexachloroacetone.^{42,43} A reaction period of 24 hours following dechlorination produced stable analytical results.

In contrast, if water samples were not dechlorinated, haloform concentrations continued to increase for several days, as others have

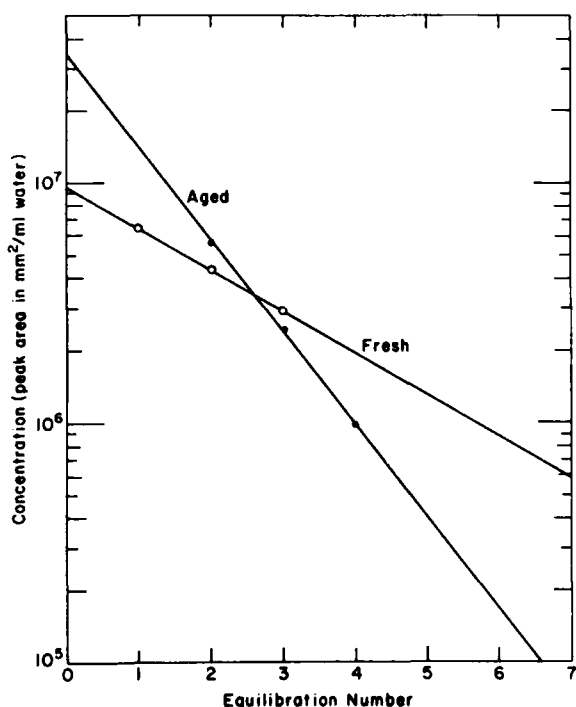


Figure 4. Chloroform concentration vs equilibration number.

noted.^{22,44,45} Data for Hanover tap water collected on 20 February 1979 and analyzed 0, 24, 48 and 72 hours after collection (without dechlorination) are shown in Table 1. Chloroform concentrations increased by a factor of >4 and bromodichloromethane by a factor of 3 in the first 24 hours. This instability of haloform precursors has made analysis for haloforms somewhat method-specific^{29,46} and has made it difficult to compare results obtained by different methods.

By the time tap water had passed the CRREL primary sewage facility, considerable reduction in haloform concentration had occurred. Analysis of fresh tap water collected on 18 January 1979 indicates a conservative estimate of 67%, not taking into account aging effects in the sewer system. Volatile losses in the sewer and primary clarifier may account for this reduction.^{17,47,48}

Unchlorinated primary wastewater applied to two prototype land treatment test cells showed undetectable levels of the haloforms (<0.2 ppb) in water after percolation through 5 feet of soil (Table 1). Details of the prototype land treatment system are available elsewhere.⁴⁹ The results obtained by multiple equilibration analysis were confirmed independently by purge and trap analysis on samples of wastewater and percolate taken later in 1979.⁵⁰

Table 1. Determination of halocarbons in some water and treated effluents by multiple equilibration analysis.

Sample	Date	Concentration (ppb)				
		CCL ₄	CHCl ₃	C ₂ H ₃ Cl ₃	C ₂ Cl ₄	CHBrCl ₂
Tap water, Hanover, N.H., fresh	1/18/79	b.d.	36.0	b.d.	b.d.	2.5
Tap water, Hanover, N.H., fresh	2/12/79	0.007	7.3	b.d.	b.d.	0.68
Tap water, Hanover, N.H., fresh	2/13/79	0.008	21.0	0.22	b.d.	1.6
Tap water, Hanover, N.H., fresh	2/15/79	b.d.	16.0	b.d.	b.d.	1.2
Tap water, Hanover, N.H., fresh	2/20/79	0.009	14.0	b.d.	b.d.	1.0
Tap water, Hanover, N.H., aged 24 hr	2/20/79	0.014	62.0	b.d.	b.d.	2.8
Tap water, Hanover, N.H., aged 48 hr	2/20/79	0.014	75.0	b.d.	b.d.	3.8
Tap water, Hanover, N.H., aged 72 hr	2/20/79	0.014	63.0	b.d.	b.d.	3.2
Primary Effluent, CRREL	1/19/79	0.011	12.0	b.d.	0.15	0.32
Percolate, Test Cell 1, CRREL	1/19/79	b.d.	n.a. [†]	b.d.	b.d.	b.d.
Percolate, Test Cell 6, CRREL	1/19/79	0.005	n.a.	b.d.	0.003	b.d.
Percolate, Test Cell 1, CRREL	2/15/79	b.d.	b.d.	b.d.	b.d.	b.d.
Percolate, Test Cell 6, CRREL	2/15/79	b.d.	b.d.	b.d.	b.d.	b.d.

* b.d. = below detection.

† n.a. = no analysis.

CONCLUSIONS

Multiple equilibration headspace analysis with electron capture gas chromatography was found to be a useful technique for identifying and determining halocarbons in water samples. Some of its advantages over purge and trap, solvent extraction, direct injection, resin sorption, and conventional headspace analysis are its sensitivity, speed, simplicity, power as an identification tool and potential as an absolute method requiring no external or internal calibration. This method is effective in identifying halocarbons associated with chlorination of water and wastewater and could readily be applied to monitor compliance with the EPA's 100-ppb standard for total trihalomethanes in finished water.

LITERATURE CITED

1. Rook, J.J. (1974) Formation of haloforms during chlorination of natural water. Water Treatment and Examination, vol. 23, no. 2, p. 234-243.
2. Bellar, T.A., J.J. Lichtenberg and R.C. Kroner (1974) The occurrence of organohalides in chlorinated drinking water. Journal of the American Water Works Association, vol. 66, p. 703-706.
3. Jolly, R.L. (1974) Determination of chlorine-containing organics in chlorinated sewage effluents by coupled ^{36}Cl tracer-high resolution chromatography. Environmental Letters, vol. 7, p. 321-340.
4. Glaze, W.H., J.E. Henderson, J.E. Bell and V.A. Wheeler (1973) Analysis of organic materials in wastewater effluents after chlorination. Journal of Chromatographic Science, vol. 11, p. 580-584.
5. Bunn, W.W., B.B. Haas, E.R. Deane and R.K. Kleopfer (1974) Formation of trihalomethanes by chlorination of surface water. Environmental Letters, vol. 10, no. 3, p.205-214.
6. Jolley, R.L., ed. (1978) Water chlorination environmental impact and health effects, vol. 1. Ann Arbor, Michigan: Ann Arbor Science.
7. Jolley, R.L., H. Gorchev, and D.H. Hamilton, eds. (1978) Water chlorination environmental impact and health effects, Vol. 2. Ann Arbor, Michigan: Ann Arbor Science.
8. Stevens, A.A. and J.M. Symons (1977) Measurement of trihalomethane and precursor concentration changes. Journal of the American Water Works Association, vol. 69, no. 10, p. 546-554.
9. Harms, L.L. and R.W. Looyenga (1977) Chlorination adjustment to reduce chloroform formation. Journal of the American Water Works Association, vol. 69, no. 5, p. 258-263.

10. Norman, T.S., L.L. Harms and R.W. Looyenga (1980) The use of chloramines to prevent trihalomethane formation. Journal of the American Water Works Association, vol. 72, no. 3, p. 176-180.
11. U.S. Environmental Protection Agency(1980) Water treatment process modifications for trihalomethane control and organic substances in the Ohio River. Report No EPA-600/2-80-028, March.
12. Rook, J.J. (1976) Haloforms in drinking water. Journal of the American Water Works Association, vol. 68, p. 168-172.
13. Fung, M.C. (1978) Reduction of haloforms in drinking water supplies. Ontario Ministry of the Environment Report No. 69, September.
14. Westrick, J.J., M.D. Cummins, and J.M. Cohen (1978) Breakpoint chlorination/activated carbon treatment: effect on volatile halogenated organics. U.S. Environmental Protection Agency Report, EPA-600/2-78-165, September.
15. McCarty, P.L. (1980) Organics in water - an engineering challenge. Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, vol. 106, p. 1-17.
16. Houel, N., F.H. Pearson and R.E. Selleck (1979) Air stripping of chloroform from water. Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, vol. 105, p. 777-781.
17. Jenkins, T.F., D.C. Leggett and C.J. Martel (1980) Removal of volatile trace organics from wastewater by overland flow land treatment. Journal of Environmental Science and Health, vol. A15, no. 3, p. 211-224.
18. Suffet, I.H., L. Brenner, J.T. Coyle, and P.R. Cairo (1978) Evaluation of the capacity of granulated activated carbon and XAD-2 resin to remove trace organics from treated drinking water. Environmental Science and Technology, vol. 12, p. 1315-1322.
19. Control of organic chemical contaminants in drinking water (1978) Federal Register, vol. 43, p. 5755, Feb. 9.
20. Bellar, T.A. and J.J. Lichtenberg (1974) Determining volatile organics at microgram per liter levels in water by gas chromatography. Journal of the American Water Works Association, vol. 66, p. 739-744.
21. Grote, J.O. (1975) Apparatus for concentration of volatile organic pollutants in water. American Laboratory, vol 7, no. 3, p. 47-50.
22. Kissinger, L.D. and J.S. Fritz (1976) Analysis of drinking water for haloforms. Journal of the American Water Works Association, vol. 68, p. 435-437.
23. Renberg, L. (1978) Determination of volatile halogenated hydrocarbons in water with XAD-4 resin. Analytical Chemistry, vol. 50, no. 13, p. 1836-1838.

24. Richard, J.J. and G.A. Junk (1977) Liquid extraction for the rapid determination of halomethanes in water. Journal of the American Water Works Association, vol. 69, p. 62-64.
25. Mieure, J.P. (1977) A rapid and sensitive method for determining volatile organohalides in water. Journal of the American Water Works Association, vol. 69, no. 1, p. 60-62.
26. Van Rensburg, J.F.J., J.S. van Huyssteen, and A.J. Hassett (1980) A semi-automated technique for the routine analysis of volatile organo-halogens in water purification processes. Water Research, vol. 12, p. 127-131.
27. Fujii, T. (1977) The determination of traces of organohalogen compounds in aqueous solution by direct injection gas chromatography - mass spectrometry and single ion detection. Analytica Chimica Acta, vol. 92, p. 117-122.
28. Nicholson, A.A. and O. Meresz (1975) Analysis of volatile halogenated organics in water by direct aqueous injection-gas chromatography. Bulletin of Environmental Contamination and Toxicology, vol. 14, no. 4, p. 453-456.
29. Pfaender, F.K., R.B. Jonas, A.A. Stevens, L. Moore, and J.R. Hass (1978) Evaluation of direct aqueous injection method for analysis of chloroform in drinking water. Environmental Science and Technology, vol. 12, no. 4, p. 438-441.
30. Kaiser, K.L.E. and B.G. Oliver (1976) Determination of volatile halogenated hydrocarbons in water by gas chromatography. Analytical Chemistry, vol. 48, p. 2207-2209.
31. Peit, G.J., P. Slingerland, F.E. de Grunt, M.P.M. van de Henval, and B.C.J. Zoeteman (1978) Determination of very volatile halogenated organic compounds in water by means of direct head-space analysis. Analytical Letters, vol. 11, no. 5, p. 437-448.
32. Morris, R.L. and L.G. Johnson (1976) Agricultural runoff as a source of halomethanes in drinking water. Journal of the American Water Works Association, vol. 68, p. 492-494.
33. Helz, G.R. and R.Y. Hsu (1978) Volatile chloro- and bromocarbons in coastal waters. Limnology and Oceanography, vol. 23, no. 5, p. 858-869.
34. McAuliffe, C.D. (1971) GC determination of solutes by multiple phase equilibration. Chemical Technology, vol. 1, p. 46-51.
35. Dilling, W.L. (1977) Interphase transfer processes II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solution. Comparisons with theoretical predictions. Environmental Science and Technology, vol. 11, p. 405-409.

36. Mackay, D. and P.J. Leinonen (1975) Rate of evaporation of low-solubility contaminants from water bodies to the atmosphere. Environmental Science and Technology, vol. 9, p. 1178-1180.
37. Lovelock, J.E., E.R. Adlard, and R.J. Maggs (1971) Gas phase coulometry by thermal electron attachment. Analytical Chemistry, vol. 43, p. 1962-1965.
38. Lillian, D. and H.B. Singh (1974) Absolute determination of atmospheric halocarbons by gas phase coulometry. Analytical Chemistry, vol. 46, no. 8, p. 1060-1063.
39. Thompson, G.M. and J.M. Hayes (1979) Trichlorofluoromethane in groundwater -- A possible tracer and indicator of groundwater age. Water Resources Research, vol. 15, no. 3, p. 546-554.
40. Morris, J.C. (1978) The chemistry of aqueous chlorine in relation to water chlorination. In Water Chlorination Environmental Impact and Health Effects, (R.L. Jolley, ed.). Vol. 1, p. 21-35. Ann Arbor, Michigan: Ann Arbor Science.
41. Morris, J.C. (1975) Formation of halogenated organics by chlorination of water supplies. U.S. Environmental Protection Agency Report, 600/1-75-002, March.
42. Glaze, W.H. and J.E. Henderson (1975) Formation of organochlorine compounds from the chlorination of a municipal secondary effluent. Journal of the Water Pollution Control Federation, vol. 47, p. 2511-2515.
43. Suffet, I.H., L. Brenner and B. Silver (1976) Identification of 1,1,1-trichloroacetone (1,1,1-trichloropropanone) in two drinking waters: a known precursor in haloform reaction. Environmental Science and Technology, vol. 10, no. 13, p. 1273-1275.
44. Stevens, A.A., C.J. Slocum, D.R. Seeger, and G.G. Roebeck (1976) Chlorination of organics in drinking water. Journal of the American Water Works Association, vol. 68, p. 615-620.
45. Bellar, T.A. and J.J. Lichtenberg (1979) Semiautomated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In Measurement of Organic Pollutants in Water and Wastewater, (C.E. van Hall, ed.). P. 108-129. Philadelphia, Pennsylvania: American Society for Testing and Materials.
46. Nicholson, A.A., O. Meresz, and B. Lemyk (1977) Determination of free and total potential haloforms in drinking water. Analytical Chemistry, vol. 49, p. 814-819.

47. Jenkins, T.F., D.C. Leggett, C.J. Martel, R.E. Peters and C.R. Lee (1980) Toxic volatile organics removal by overland flow land treatment. Proceedings of the Research Symposia, 53rd Annual Conference of the Water Pollution Control Federation.
48. Cohen, Y., W. Cocchio, and D. Mackay (1978) Laboratory study of liquid-phase controlled volatilization rates in presence of wind waves. Environmental Science and Technology, vol. 12, p. 553-558.
49. Iskandar, I.K., R.S. Sletten, D.C. Leggett, and T.F. Jenkins (1976) Wastewater renovation by a prototype slow infiltration land treatment system. CRREL Report 76-19.
50. Jenkins, T.F. (1980) Unpublished data.

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